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Natural polysaccharides as electroactive polymers

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Abstract Electroactive polymers (EAPs), a new class of materials, have the potential to be used for applications like biosensors, environmentally sensitive membranes, artificial muscles, actuators, corrosion protection, electronic shielding, visual displays, solar materials, and components in high-energy batteries. The commercialization of synthetic EAPs, however, has so far been severely limited. Biological polymers offer a degree of functionality not available in most synthetic EAPs. Carbohydrate polymers are produced with great frequency in nature. Starch, cellulose, and chitin are some of the most abundant natural polymers on earth. Biopolymers are a renewable resource and have a wide range of uses in nature, functioning as energy storage, transport, signaling, and structural components. In general, electroactive materials with polysaccharide matrices reach conductance levels comparable with synthetic ion-conducting EAPs. This review gives a brief history of EAPs, including terminology, describes evaluation methods, and reports on the current progress of incorporating polysaccharides as matrices for doped, blended, and grafted electroactive materials.

Introduction

Scope

Traditionally, polymeric materials are used as insulators. Electroactive polymers (EAPs), a new class of materials, received recent attention from academia and industry due to their potential for applications such as biosensors, artificial muscles, actuators, corrosion protection, electronic shield-

ing, environmentally sensitive membranes, visual displays, solar materials, and components in high-energy batteries (Bakhshi 1995; Zhang et al. 2000). The commercialization of synthetic EAPs, however, is severely limited due to limitations in production and mechanical properties.

Biological polymers (biopolymers) offer a degree of functionality not available in most synthetic EAPs. Carbohydrate polymers (polysaccharides) are produced with great frequency in nature. Starch, cellulose, and chitin are some of the most abundant natural polymers on earth. Biopolymers are a renewable resource and have a wide range of uses, functioning as energy storage, transport, signaling, and structural components. Agriculture-based biopolymers could have an economic advantage over synthetic, petroleum-based products in the future. This review gives a brief history of EAPs, including terminology, describes evaluation methods, and reports on the current progress of incorporating polysaccharides as matrices for doped, blended, and grafted electroactive materials.

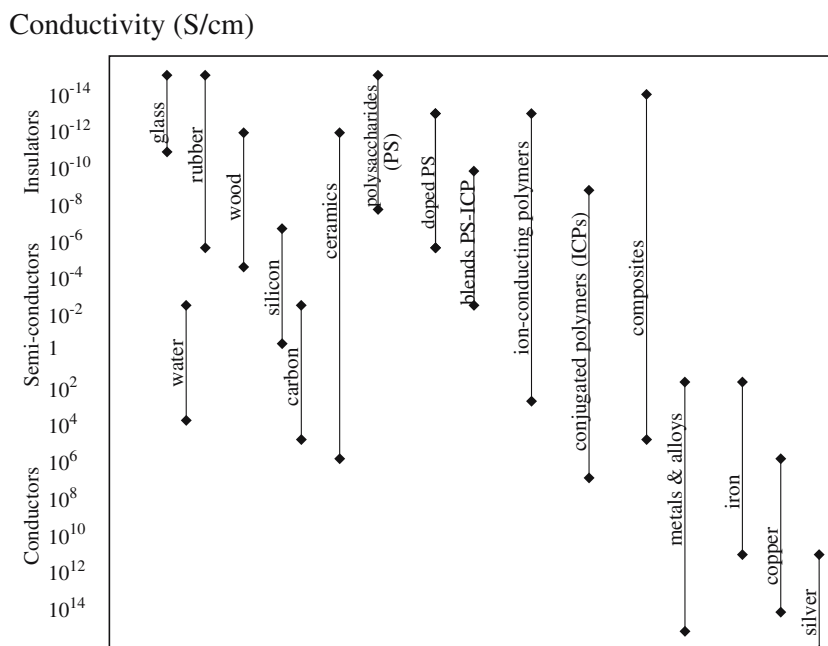
History

The first polymer shown to conduct electricity was poly(acetylene) (Shirakawa et al. 1977). The 2000 Nobel Prize in Chemistry¹ was shared between chemist Alan MacDiarmid (USA, New Zealand), physicist Alan Heeger (USA), and chemist Hideki Shirakawa (Japan), based on the discovery of conductive organic polymers. Working together at the University of Pennsylvania in 1977, they were the key researchers in the formulation of conductive poly(acetylene) and contributed to the development of this scientific field. The occurrence of conductivity in plastic, long considered an insulator, at levels comparable with conventional metals was completely unexpected and led to an expanding research field. Since conducting polyacetylene was discovered, a number of other conducting polymers (or more generally, electroactive polymers) with unique properties have been developed.

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¹ <http://www.nobel.se/chemistry/laureates/2000/>

Fig. 1 Conductivity ranges for selected materials, including biobased electroactive polymers



Electroactive polymers are usually classified into two categories, polymer electrolytes and conducting polymers, depending on the mode of electron transport. Conducting polymers are polymeric materials that are electron conductors by virtue of π electrons via conjugated double bonds and are referred to as intrinsically conducting polymers (ICPs). Polymer electrolytes achieve their functional conductance by ion conduction. Different salts may be dissolved into the solid polymer (usually with a small amount of solvent), creating a solid polymer electrolyte. The dissociated ions are free to move within the matrix and can conduct electricity under applied voltage, just as they do in conventional solutions. ICPs may have their conductance increased by introducing ionic species into the matrix (called doping), allowing for oxidation–reduction (redox) reactions to occur as well as electronic and ionic conduction. Figure 1 shows a variety of resistive, semiconductive, and conductive materials.

One of the attractions of plastic conductors is their combination of electrical properties with mechanical properties. Synthetic EAPs are generally insoluble, disordered, and intractable. The morphology is determined by chemical and electrochemical growth conditions and cannot be modified after deposition. This limits applications and industrial scale-up processes. Current efforts are aimed at modifying synthetic EAPs with functional groups or blending with other polymers to create a balance between functional levels of electroactivity and desirable mechanical properties.

Terminology

Materials can be classified either as a conductor, insulator, or semiconductor, based on the structure of electron energy levels (Fig. 2). Each material possesses a conductance and

valence band for electrons; and the energy difference between these two bands (energy gap or band gap) determines the resistance of the material to the passage of electrical current (Schott and Nechtschein 1994). The conduction band contains “free” electrons that have been excited out of the valence band. Free electrons are allowed to move and conduct electricity when an external electric field is applied.

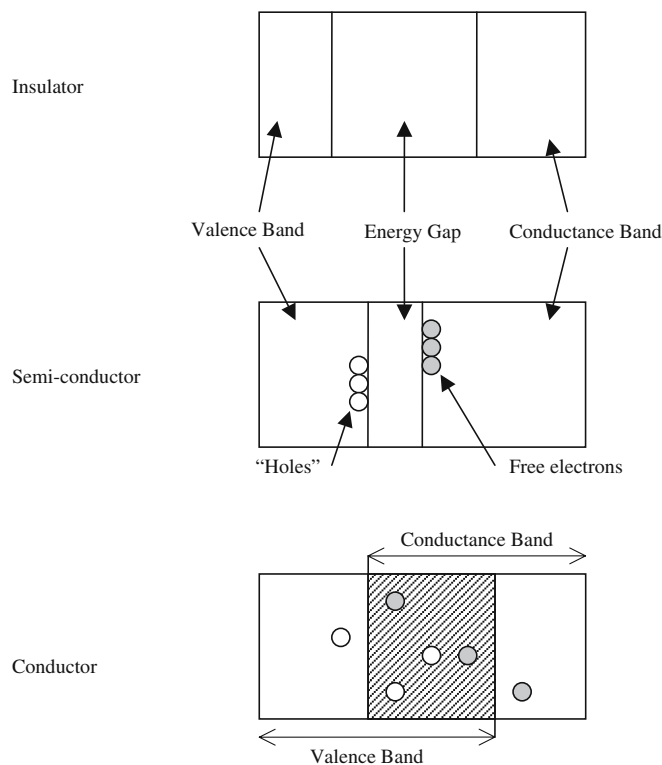


Fig. 2 Schematic of energy gaps in insulators, semiconductors, and conductors

In conductors, the conductance and valence band overlap. Thus there is no energy gap, so any energy added is sufficient to propel electrons out of the valence band into the conduction band, allowing current to flow. Insulators have a large energy gap between the valence and conduction bands, making it difficult for electrons to leave the valence band and restricting current flow through the material. Semiconductors have distinct valence and conduction bands, but the energy gap is not as large as with insulators. With the application of an external electric field, electrons are excited more easily out of the valence band into the conduction band and the number of free charge carriers is influenced by the supplied energy, so that the conductivity can be influenced by external potentials.

Electrical resistance is a property in which a material resists the flow of electrical current (Ku and Leipins 1987). Ohm's law,

$$R = E/I, \quad (1)$$

defines the resistance, R (ohms), as the ratio of voltage, E (volts), to current, I (amperes). Conductance is the reciprocal of resistance and, therefore, the ease with which an electric current flows through the material. The standard unit of conductance is the siemens (abbreviated S), formerly known as the mho (a reciprocal ohm). When a current of 1 A passes through a component across which a voltage of 1 V exists, then the conductance of that component is 1 S. Conductance (S/cm) is generally reported as a bulk property in EAPs.

For ion-conducting materials, the conductance of the system is dependent on the polymer matrix (including moisture), the concentration of ionic species, the mobility of the ions, the valence of the ionic species, and temperature (Linford 1993). For simplicity, one can assume the electronic contribution of the polymer matrix is zero and ionic mobility is predominant, by evaluating materials normalized to a control sample. Thus, the conductance of an ion-conducting material can generally be expressed as:

$$\sigma(T) = \sum n_i q_i \mu_i \quad (2)$$

where σ is the conductance of the material at a certain temperature (T), n is the number of charge species per unit mole, q is the net charge of each species, and μ is the ion mobility of each species. In the case of doped ICPs, Eq. 2 becomes more complex, as account must be taken of electronic conductivity, redox reactions due to the reactivity of the polymer matrix, and ion mobility.

Ionic conductivity in polymers is directly related to the segmental motion of polymer chains in semicrystalline specimens (Berthier et al. 1983). The conductivity pathway can be attributed to the mobility of ions along a flexible polymer backbone utilizing transient crosslinks (Finkenstadt and Willett 2004b; LeNest et al. 1993), a phenomenon called "chain hopping" in charge transport physics (Bakhshi 1995).

Evaluation by alternating current

Ohm's law (Eq. 1) describes the behavior of an ideal resistor; most polymers are not ideal, thus impedance is used. Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current. Impedance spectra are influenced by processes such as electron transfer, mass transport and chemical reactions. Electrochemical impedance spectroscopy (EIS) uses a small amplitude signal, usually 5–50 mV, applied over a range of frequencies (0.001–100,000 Hz). EIS measures the complex components of the impedance response of the specimen, i.e., the "real" resistance and the "imaginary" capacitance:

$$Z = E/I = Z_0 \exp(j\phi) = Z_0(\cos \phi + j \sin \phi) \quad (3)$$

The impedance is therefore expressed in terms of a magnitude, Z_0 , and a phase shift, ϕ . The impedance is plotted (Bode plot) with log frequency on the x -axis and both the absolute value of the impedance ($|Z|=Z_0$) and phase shift (ϕ) on the y -axis. The impedance of a material acting as a resistor is independent of frequency and has only a real component. Because there is no imaginary impedance, the current through a resistor is always in phase with the voltage and:

$$R = Z. \quad (4)$$

EIS data is generally analyzed in terms of an equivalent circuit model. Most of the circuit elements in the model are common electrical elements, such as resistors, capacitors, and inductors. The analyst tries to find a model whose impedance matches the measured data. Modern EIS analysis uses a computer to find the model parameters that give the best agreement between a model's impedance spectrum and a measured spectrum. For most EIS data analysis software, a nonlinear least squares fitting algorithm is used (Scully et al. 1993). Cyclic voltammetry (CV) allows the study of electrochemical activity, especially redox processes, of biological molecules where diffusion predominates. CV involves potentiometric measurements using pairs of chemical electrodes and driving the reaction by controlling the voltage. In typical CV, a solution component is electrolyzed (oxidized or reduced) by placing the solution in contact with an electrode surface and then making that surface sufficiently positive or negative to force electron transfer. Polymer films are cast onto the electrode surface and the experimental data is collected using standardized electrolyte solutions and electrode potentials.

Evaluation by direct current

A direct-current resistance technique has been shown to accurately measure resistance in polysaccharide films (Finkenstadt and Willett 2004a). This test method involves a direct-current procedure for surface and volume resis-

tance/resistivity of powders, pellets, and thin sheets and conforms to the standards established by ESD S11.11 and ASTM D 257 (American Society of Testing Materials 1993). Resistance is directly measured, using a defined electrode configuration (concentric ring electrode), test voltage (0.75 V), and environmental conditions. This method is used for rapid screening of newly developed electroactive materials. In ion-conducting materials, the conductance is described by Eq. 2. The Hall effect (subject of another Nobel Prize²) utilizes quantum mechanics to describe electrical transport by defining the carrier density, n , and the mobility (μ) of a conducting species. The basic principle for the Hall Effect is the Lorentz force. When an electron moves along an applied magnetic field, it experiences a force acting perpendicular to both directions and moves in response to this force and the force applied by the internal electric field. Electrons subject to Lorentz force initially drift away from the current line, resulting in excess electrical charge on one side of the sample and giving rise to the Hall voltage, a measure of the potential drop across the sample normal to the applied voltage. The most used method in the semiconductor industry for measuring the Hall effect is the van der Pauw method (van der Pauw 1958) which shows that, for an arbitrary shaped sample of thickness, d :

$$\exp(-\pi d R_{ab,cd}/\rho) + \exp(-\pi d R_{bc,ad}/\rho) = 1 \quad (5)$$

where ρ is the bulk resistance and $R_{ab,cd}$ is determined by dividing the potential difference in voltage (c, d) traveling perpendicular to the current (a, b). $R_{bc,ad}$ is defined in a similar manner. Measuring the Hall voltage allows the calculation of resistance, density of charge carriers, and mobility of charge carriers for homogeneous bulk materials.

EAPs and their applications

Starch

Starch is composed of a mixture of linear and branched polysaccharides (Fig. 3a). Amylose is a linear polymer of $\alpha(1,4)$ -linked anhydroglucose units (AGU). Amylopectin is a highly branched polysaccharide composed of linear $\alpha(1,4)$ -AGU chains with branch-points being $\alpha(1,6)$ -linkages. While starch is packaged into granules in its native state, the properties of starch materials are exhibited when the granular structure is broken down by mechanical and thermal means. Thermoplastic starch (TPS), produced by reactive extrusion, can be doped with metal halides (MX; Finkenstadt and Willett 2001, 2004b). The amount of moisture in the system affects both the mobility of polymer and ion within the system and the quality of the physical properties of TPS (Finkenstadt and Willett 2004a). Finkenstadt and Willett (2004b) showed that, while moisture contributes to the overall bulk conductivity of TPS, there is a point (around 25–30% moisture content) at which

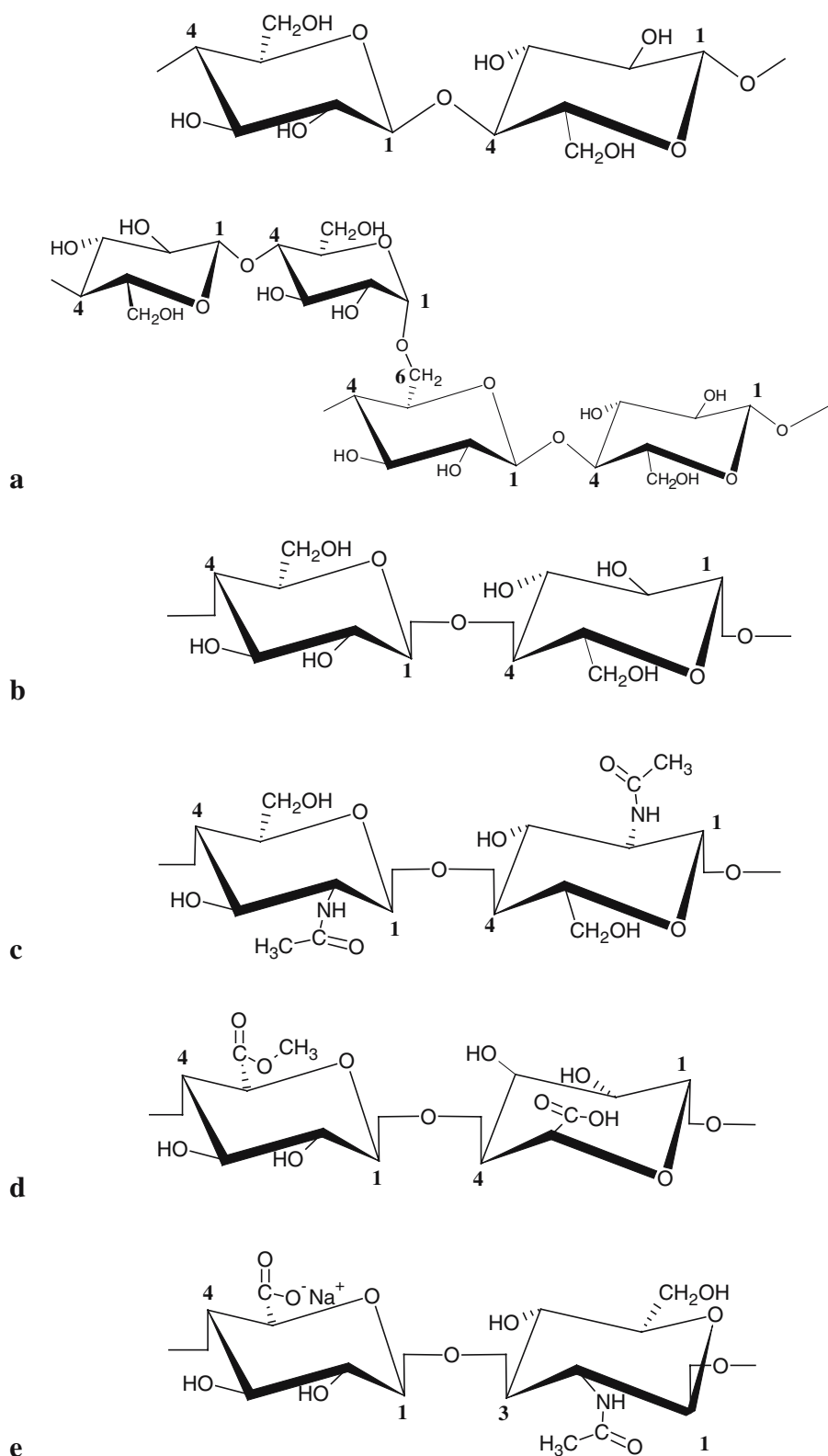
water does not contribute. Therefore, the effect of MX on physical properties and electroactivity could be determined by keeping the moisture (and plasticizer) content constant. More importantly, the concentration of MX was kept on a molar basis to AGU rather than on a weight basis, so that the effect of charge species could be examined. TPS with 30% moisture content exhibits a conductance of 10^{-9} – 10^{-11} S/cm, as measured by direct-current methods. Starch is naturally insulative and its proton mobility is low (Lopes et al. 2003). Upon doping with MX (NaCl, NaI, LiCl, LiI), the material exhibits conductance between 10^{-5} S/cm and 10^{-6} S/cm. At the same molar ratio, different mixtures of TPS-MX exhibit different levels of conductance. The addition of MX affects the mechanical properties of TPS. In general, the films become more flexible as the amount of MX increases, probably due to the plasticizing effect of large anions (LeNest et al. 1993). Lopes et al. (2003) gelatinized amylopectin-rich starch with water on a hotplate. The solution was combined with glycerol, mixed with LiClO_4 , cast onto Teflon plates, and allowed to dry. The cationic species, Li^+ , was balanced on a molar basis to the hydroxyl groups present in the starch–glycerol mixture, such that $[\text{Li}]/[\text{OH}]$ was 6 or 8. The starch–glycerol– LiClO_4 films exhibited conductances of around 10^{-5} S/cm. Chemical modification of starch and cellulose with poly(ethylene oxide) (PEO) grafts showed that the degree of plasticization and glass transition (T_g) of electroactive biopolymers is important to optimize electroactivity (Pawlicka et al. 2002).

Cellulose

Cellulose is a $\beta(1,4)$ -linked D-glucan (Fig. 3b). Cellulose xanthate was dissolved in water, mixed with polyethylene glycol (PEG), and precipitated with ethanol (Nada et al. 2004). The electrical conductance of the PEG-plasticized cellulose xanthate depended on the presence of free ions, since the electron conduction was essentially zero. Hydroxyethyl cellulose (HEC) was blended with PEO to form good films, which is essential for some applications (Regiani et al. 2001; Schoenenberger et al. 1995). HEC was also grafted with propylene oxide (PPO) and then blended with PEO (Fig. 4a) to form crosslinked polyether networks (LeNest et al. 1993). The resulting insoluble films were doped with lithium bis(trifluoromethanesulfo) imide [$\text{LiN}(\text{CF}_3\text{SO}_2)_2$]. This system took the advantages of the film-forming properties of cellulose, the conductivity of PPO/PEO, and the ionic conductivity provided by $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. In this system, the Li^+ complexed preferentially with the PEO, as opposed to the PPO sidechains or cellulose hydroxyl groups. A correlation was found to exist between the concentration of dopant and the decrease in T_g and concurrent rise in conductance of the doped PEO-blended HEC-g-PPO, up to a critical concentration of dopant. The conductance approached 10^{-4} S/cm at the highest salt concentration. In other work, the ion mobility of HEC and PEO blends doped with LiClO_4 was measured by ^1H and ^7Li nuclear magnetic resonance (NMR; Tambelli et al. 2001). The parameters

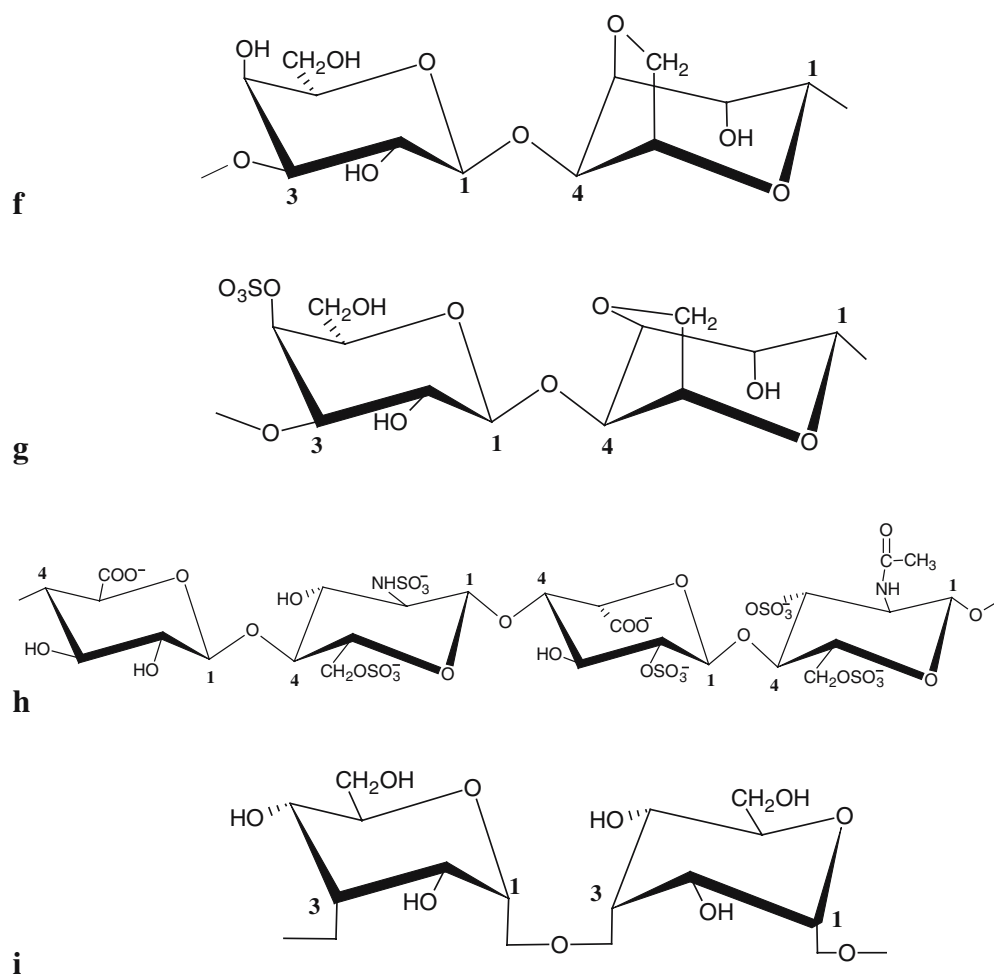
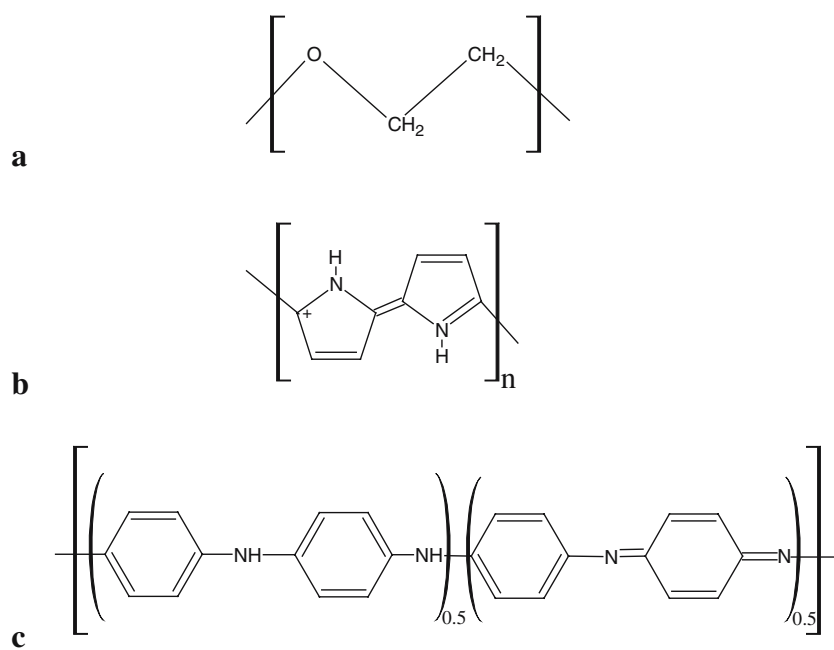
² <http://www.nobel.se/physics/laureates/1998/>

Fig. 3 Haworth structures of polysaccharides: **a** amylose and amylopectin, **b** cellulose, **c** chitin, **d** pectin, **e** hyaluronic acid, **f** agarose, **g** κ -carrageenan, **h** heparin, **i** pullulan



estimated from the NMR data indicated that the mobility of Li^+ is comparable with PEO- LiClO_4 polymer electrolytes. Kim and coworkers studied different papers made from hard woods, soft woods, bacterial cellulose, rice paper, and cellophane for use as actuators. Cellophane, regenerated

cellulose, is a piezoelectric material that transforms electrical energy to mechanical energy (Je and Kim 2004; Kim et al. 2002). A blend of cellulose xanthate and PEG achieved a conductivity around 10^{-5} S/cm (Nada et al. 2004). Cellulose dialysis tubing was coated with polypyrrole (PPy) and

Fig. 3 (continued)**Fig. 4** Chemical structures of selected conductive polymers: **a** poly(ethylene oxide), **b** poly(pyrrole), and **c** poly(aniline)

polyaniline (PANI; see Fig. 4b, c) to achieve conductivity values around 0.1–1.0 S/cm. However, the typical conductivity values for PPy and PANi are within the same range (Humphrey et al. 1990). Cellulose, in this case, served as a flexible substrate for coating ICPs (Weiss et al. 1989).

Chitosan

Chitosan is the *N*-deacetylated form of chitin with the repeat unit $\beta(1,4)$ -linked 2-acetoamido-2-deoxy-D-glucose (Fig. 3c). Because of its functional groups, chitosan has many potential applications, including electroactive polymers. In recent work, chitosan was plasticized (Wan et al. 2003) and doped with sodium perchlorate (NaClO_4 ; Subban et al. 1996), sodium iodide (NaI ; Subban and Arof 1996), lithium trifluoromethanesulfonate (LiCF_3SO_3 ; Osman et al. 2001), and lithium acetate (LiCH_3CO_2 ; Yahya and Arof 2002). Conductivity values, obtained from complex impedance, for doped chitosan films were around 10^{-5} – 10^{-6} S/cm, depending on salt type and amount. Control films of “dry” chitosan have a conductance of 10^{-10} S/cm (Wan et al. 2003). Hydrated films of chitosan achieved a conductance of 10^{-4} S/cm. Film were immersed in water for 1 h or 24 h before being tested. After 1 h, the material reached saturation point and no increase in conductivity was observed after 24 h of immersion. They attributed the ionic conductivity of the undoped chitosan films to hydroxyl ions (Wan et al. 2003). Since the free amino groups are partially protonated by water freeing $[\text{OH}^-]$ to move, increasing deacetylation should yield higher conductivity. This was not observed, but the crystallinity of the material increased with deacetylation, preventing mobile species from migrating under AC signal, due to rigid polymer chains. In all cases, the ultimate goal was to suggest the use of ion-conductive chitosan films as membranes for alkaline polymer electrolyte batteries and fuel cells. Another application for chitosan is corrosion protection. Pore resistance is a convenient way to represent corrosion protection. Pore resistance indicates the level of ionic conductivity from the electrolyte penetration into the coating, i.e. as pore resistance increases, ionic conductivity decreases. In the case of corrosion protection, penetration of corrosives (salts, moisture, etc.) is undesirable, so the conductivity imparted by ionic species (a measure of the ionic mobility) within the matrix should be low. EIS allows the evaluation of coatings designed to block corrosives from reaching the metal surface. Sugama and Cook (2000) grafted poly(itaconic acid), a synthetic water-soluble negatively charged polymer, onto chitosan in order to balance the charge of the matrix. The pore resistance in this case was around $10^6 \Omega/\text{cm}^2$ compared with $5.0 \times 10^3 \Omega/\text{cm}^2$ for the uncoated aluminum substrate.

Pectin

Pectin and starch were separately grafted with polyorganosiloxane (POS) and blended with an antimicrobial agent (Sugama 1995; Sugama and DuVall 1996). Pectin is a

polygalacturonic acid methyl ester with varying degrees of methylation (Fig. 3d). The copolymer mixture was then applied to aluminum substrates and evaluated for resistance to water, microbial attack, and corrosion protection. Pectin-g-POS was thermally more stable than pectin, was less susceptible to moisture due to a loss of hydrophilic groups, and imparted greater corrosion protection. The impedance (Z) of bare aluminum is approximately 3.0 – $5.0 \times 10^3 \Omega/\text{cm}^2$ at a frequency of 0.5 Hz. Aluminum coated with pectin alone had a slightly higher pore resistance than the bare aluminum surface. However, aluminum coated with pectin-g-POS or starch-g-POS showed an increase of at least one order of magnitude greater than bare aluminum. In addition, the incorporation of an antimicrobial agent into the graft played a role in the overall susceptibility of the coating to degradation by water or microbes. There is greater corrosion protection, due both to favorable interactions of POS with aluminum oxide layers on the metal surface and to the reduced hydrophilic nature of the polysaccharide matrix.

Hyaluronic acid

Collier et al. (2000) coupled the biocompatibility of hyaluronic acid (Fig. 3e) with the electroactive properties of PPy for tissue replacement and repair therapies. Biomaterials for tissue engineering must have structural support for tissue growth and trigger specific cell responses. PPy (Fig. 4b) is an ICP and generally requires a negatively charged counterion to elicit full conductivity. Hyaluronic acid is a negatively charged glycosaminoglycan and was chosen for its biocompatibility and known activity in wound healing and tissue regeneration. Hyaluronic acid was blended with PPy in a single thin layer (PPy-HA) or deposited on a layer of PPy-poly(styrenesulfonate) (PSS). The DC conductance, measured by the van der Pauw (1958) method, of the control sample of PPy-PSS had a conductivity of 9.3 S/cm while the PPy-HA blend had significantly lower conductance (3.08×10^{-3} S/cm, four orders of magnitude less). The bilayer (PPy-HA plus PPy-PSS) had a similar conductance (8.02 S/cm). The conductance of the control layer was similar to the conductance of PPy reported in the literature. The authors correctly note that since the thickness of the PPy-HA layer of the bilayer was $0.05 \mu\text{m}$ compared to the blend's thickness of $0.15 \mu\text{m}$ or $2.0 \mu\text{m}$, the conductance exhibited by the bilayer was most likely influenced by the thicker ($0.1 \mu\text{m}$ or $1.95 \mu\text{m}$) PPy-PSS substrate. The technique used could be expected to exhibit the limitations described. Nevertheless, the laminate as a whole was conductive and the PPy-HA layer exhibited the characteristic biological reactivity and biocompatibility expected of HA. The PPy-HA/PPy-PSS laminate exceeded the biological responses (such as morphology, HA activity, cell compatibility, nontoxicity, increased vascularization) of the control sample of PPy-PSS. It was noted, though, that HA is rapidly degraded in vivo and therefore further studies to crosslink or anchor HA into PPy are needed.

Agarose and carrageenan

Agarose (Fig. 3f) and κ -carrageenan (Fig. 3g) were doped with potassium salts (KCl, KNO₃, KI), cesium chloride (CsCl), and calcium chloride (CaCl₂; Ueno et al. 2004). Polysaccharide was added to 0.1 M electrolyte solutions up to 5% w/w. The resulting gels with “excess water” were measured for hardness (gel strength) and resistivity by EIS. For 2% w/w or less, the resistivity of the complexed gel was similar to that of the electrolyte solution. They noted an increase in conductivity as more polysaccharide was added up to 3% w/w and then noted a decrease in conductivity. As more polysaccharide was added, the gel strength increased. They interpreted this behavior by linking the diffusion of ions and the ionic conductivity with the growth of a three-dimensional matrix. This is supported by traditional polysaccharide solution studies (Ciszkowska et al. 2000). Agarose and carrageenan have been used as matrices for solar cells (Kaneko and Hoshi 2003) and blended with PPy and PANi (Humphrey et al. 1990).

Cyclodextrin

Inclusion complexes were formed between cyclodextrin and polyaniline (Yoshida et al. 1999). Cyclodextrins are cyclic molecules with six to eight glucose molecules and have been shown to be able to form molecular wires (“necklaces”) with linear polymers. Results from frequency-domain electric birefringence indicated that PANi was completely coated by cyclodextrin necklaces, forming an insulated molecular wire where PANi molecules are separated by cyclodextrin. However, no effort was made to determine the conductance of the complex.

Gum Arabic

Gum Arabic, an arabinogalactan, was cast out of solution and exhibited a conductivity of approximately 1.5×10^{-6} S/cm after drying (Mallick and Sarkar 2000). It was determined through impedance and a transient ion current technique that Gum Arabic functioned as a proton conductor through hydronium ions (H₃O⁺).

Heparin and dextran sulfate

Heparin was incorporated into PPy in order to create an immobilized biosensor for thrombin (Zhou et al. 1999). Heparin is a linear polysaccharide of glucuronic acid and glucosamine containing sulfates (Fig. 3h). Heparin is widely known as an anticoagulant and has specific affinity for thrombin. It was shown that polyelectrolytes (such as heparin) can be incorporated in ICPs during synthesis. Cyclic voltammetry indicated that the heparin–PPy was electroactive upon oxidation/reduction in a reversible process. The primary mode of conduction was cation ex-

change—cations moving in and out of the heparin–PPy matrix to maintain charge balances during redox reactions. Cation conduction could be attributed to the large anion (i.e. heparin) immobilized in the PPy matrix. The cation conductivity of heparin–PPy was significantly more than doped PPy. The heparin retained its biological activity on the surface of the heparin–PPy blend. In separate work, heparin and dextran sulfate were blended with PPy to create hydrophilic polyelectrolytes that were able to store and release proteins (Hodgson et al. 1996). This process could be controlled by varying the potential of the charge.

Pullulan

Cyanoethylpullulan was used as a gel electrolyte in which PEO was polymerized (Yoshida et al. 2002). Pullulan is composed of $\beta(1,3)$ -linked D-glucose (Fig. 3i). The resulting conductive gels with LiBF₄ as the dopant had approximately 15% solids (85% water). Other cellulosic polysaccharides (cyanoethylcellulose, carboxymethylcellulose, cellulose acetate) were also evaluated but did not form strong gels. The pullulan–PEO gel had a conductivity of 2.4×10^{-3} S/cm, as measured by complex impedance, and had good electrochemical stability. The pullulan–PEO gel electrolyte could be used for lithium polymer battery applications.

Discussion

Methods of preparation

Water-soluble polysaccharide films are usually prepared by dissolving a small amount (usually 1–5% w/w) into purified water. In some cases, the pH is adjusted to facilitate dissolution. The solutions become viscous, are filtered, and then cast onto Teflon or glass surfaces. The self-supporting films are dried or annealed under controlled environmental conditions (temperature, relative humidity). For some applications, electrode surfaces are dip-coated with polysaccharide solutions and dried. Salts are dissolved into polysaccharide solutions before casting, to produce ion-conducting films. In some instances, polysaccharide films are soaked in an electrolyte solution to allow diffusion of ions and then dried.

For starch, films can be prepared by extrusion. Starch, a mixture of linear amylose and branched amylopectin (Fig. 3a), obtains its plastic properties upon the gelatinization and destructuring of starch granules with enough water and thermomechanical energy. Starch can be gelatinized by heating on the benchtop or cold-gelatinized with NaOH, but true thermoplastic starch (TPS) is easily obtainable through extrusion. The moisture content is usually between 30% and 50%, compared with +95% for casting films from polysaccharide solutions. TPS can be extruded into thin films or pelletized. With reactive extrusion, TPS can be derivatized, blended with salts to produce ionic conductors, or blended with ICPs in a single, continuous

process. Samples thus obtained are stored at 50% relative humidity and standard room temperature (23°C) until evaluation.

Effect of polysaccharide matrix

Natural polymers such as polysaccharides have a variety of structures that impart extensive differentiation in properties. Hydroxyl groups of the sugar rings allow for easy substitution of other functional groups. Differences in sugar composition and functional group substitution affect the three-dimensional packing of the polysaccharides and their interactions with other polymers or salts. Polysaccharides that show extensive hydrogen bonding appear to be more conductive than those that have few hydrogen bonds. Crystallinity plays a role in the polymer mobility and ion mobility of electroactive materials. Due to their hydrophilic nature, the moisture content of the electroactive material changes depending on environmental conditions.

Effect of moisture content

Biopolymers can be described as water-filled carbohydrate matrices. Their electroactivity and mechanical properties are affected by the degree of hydration (moisture content). In the case of marine polysaccharides (agarose, carrageenan), Ueno et al. (2004) did not define “excess water” or the actual moisture content of the “solid” gels. They attributed the increase in conductivity to the formation of a three-dimensional network (i.e. hardness increased) and attributed inhibited ion diffusion to the amorphous phase. In most cases (except for starch), researchers have not determined the moisture content of biobased EAPs. Finkenstadt and Willett (2004a,b) showed that, for TPS, the amount of salt added affects the moisture content of the polysaccharide film. The combination of salt and water affects the mechanical properties of the film, which in turn affects the mobility of ions and the conductivity. This can also be seen in synthetic hydrocolloid blends (Kim et al. 2000). Osman et al. (2001) noted that in chitosan, after a certain hydration level (a 1-h soak), water content does not affect conductivity. Plasticizers other than water help polymers solvate salts and increase conductance, due to increased polymer and ion mobility.

Effect of salt and salt concentration

An ongoing theme is salts that have large anions and small cations. The anions seem to have a plasticizing effect on the polymer matrix (Finkenstadt and Willett 2004b; LeNest et al. 1993). Ionic conduction is enhanced by the addition of plasticizers that aid in the dissociation of salts and allow more polymer mobility (Finkenstadt and Willett 2004b; Lopes et al. 2003). Subban (1996) explained conductance in chitosan by the weak electrolyte theory. They assume that the ion mobility term in Eq. 2 is constant and thus the

free ion concentration must dominate conductivity. The decrease in conductivity is then a reflection of the decrease in free ions within the polymer matrix. They described it as overcrowding in a fixed volume of the host material causing a restriction in ion diffusion. Subban and Arof (1996) stated it more clearly: the chitosan can only assimilate a fixed amount of dissociated cations and anions, limiting the inclusion of ionic species within the matrix. The “free ions” are ions that form transient crosslinks (complexes, chelation, hydrogen bonds) in the matrix and are mobile under applied current.

When adding a dopant salt to a matrix, the dominant energetic barrier experienced by the cation in conduction is given by the dissociation of the alkali itself. The material can be both ionically and electronically conducting. However, in most polysaccharides, conduction is due solely to the movement of a single ionic species. Which of the two terms (mobility, charge concentration) makes the dominant contribution to the conduction? One model supposes that all cations contribute to the conductivity and indicate the dominance of the mobility term but the weak electrolyte theory says that only a small fraction of the ions are contributing, at a given time, to the conduction. In most cases, there appears to be a critical limit for the concentration of ionic species and exceeding this limit has no benefit to conductivity. This can be attributed to a partitioning of ions in the matrices. Each polysaccharide repeat unit is able to complex a limited number of cations or anions. Above this critical concentration, ions are not incorporated and are excluded from the matrix.

Conclusions

Moisture content (or level of plasticizer) plays an important role in the solvation of salts by the polymer matrix, ion mobility, and polymer mobility. Most biobased EAPs are ion-conducting materials. From the seemingly contrary results and interpretations regarding the mobility of ions within ordered or disordered regions of electroactive biopolymers, one can suggest that different mechanisms are responsible for ionic conductivity, depending on polymer matrix, ionic species, strength of complexation, and amount of order in the system. Recent work concerning synthetic polymer electrolytes suggest that ion transport in crystalline polymers may be dominated by cations (small cations have larger mobility), while both cations and anions are mobile in amorphous regions (Gadjourova et al. 2001). While biobased EAPs have not achieved the level of conductance of some synthetic EAPs at this time, it is only a matter of time until they can be engineered and developed.

Future natural EAP applications

The information presented here demonstrates the viability of using naturally occurring polysaccharides for biobased EAPs in applications such as batteries, anticorrosion technology, tissue engineering, actuators, electrochromic paper,

molecular wires, and biosensors. There are major opportunities for the development of EAP biotechnology using integrated biological, chemical, and engineering approaches, with bioreactors, fermentations, and organisms specifically designed to produce electroactive biopolymers. Electroactive biopolymers have better biocompatibility and are more environmentally friendly than synthetic EAPs. Sustainability will be achieved by the tailored biosynthesis of conductive biopolymers, using plants and microbes. Biosensors and actuators will use plant or bacterial biopolymer matrices for EAPs that convert energy into either mechanical force or chemical charge or both. Grafting natural polysaccharides with ICPs in a continuous process will make the production of EAPs more economically feasible. The use of renewable resources to produce nontraditional biobased products will affect the worldwide dependence on petroleum-based and synthetic products and feedstocks.

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